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Reactions of Fuel Nitrogen Compounds under Conditions of Inert Pyrolysis

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16. ABSTRACT

The paper describes the pyrolysis of fossil fuels and model nitrogen compounds in helium in a small quartz plow reactor, as part of a study of the chemical mechanisms involved in the conversion of fuel-nitrogen compounds to nitric oxide (NO) during combustion. Hydrogen cyanide (HCN) was the major nitrogen-containing product obtained in all cases, indicating that HCN is formed during the initial pre-flame stages of combustion and is the principal intermediate in the formation of fuel NO. At a nominal residence time of 1 second, 50% decomposition of pyrrole, quinoline, benzonitrile, and pyridine occurs at 905, 910, 922, and 954 C, respectively. The fraction of the nitrogen in pyridine that is converted to HCN increases from 40% at 960 C to 100% at 1100 C. Benzonitrile produces similar amounts of HCN (49 and 82%). The HCN yields from coals and residual fuel oils increase from the range of 15-25% at 950 C to 23-42% at 1100 C. It is not possible to determine from these single-stage experiments if most of the HCN forms in the primary pyrolysis process or in secondary reactions.

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Combustion	Stationary Sources	21B
Nitrogen		07B
Fuel Nitrogen		
Nitric Oxide		07B
Chemical Mechanisms		07D
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Reactions of fuel-nitrogen compounds under conditions of inert pyrolysis

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As part of a study of the chemical mechanisms involved in the conversion of fuel-nitrogen compounds to nitric oxide during combustion, fossil fuels and model nitrogen compounds were pyrolysed in helium in a small quartz flow reactor. Hydrogen cyanide was the major nitrogen-containing product obtained in all cases indicating that hydrogen cyanide is formed during the initial pre-flame stages of combustion and is the principal intermediate in the formation of fuel nitric oxide. At a nominal residence time of one second, 50% decomposition of pyrrole, quinoline, benzonitrile and pyridine occurs at 905, 910, 922 and 954°C, respectively. The fraction of the nitrogen in pyridine that is converted to hydrogen cyanide increases from 40% at 960°C to 100% at 1100°C. Benzonitrile produces similar amounts of hydrogen cyanide (49 and 82%). The hydrogen cyanide yields from coals and residual fuel oils increase from the range of 15–25% at 950°C to 23–42% at 1100°C. It is not possible to determine from these single-stage experiments if most of the hydrogen cyanide forms in the primary pyrolysis process or in secondary reactions.

One class of pollutants that is of concern, both in its own right and as an intermediate in the production of photochemical smog, is nitrogen oxides (NO_x). About 99% of the NO_x generated by man's activities is produced during the combustion of fossil fuels and nearly all is produced as nitric oxide. Of that, mobile and stationary sources each contribute approximately 50%; however, some projections indicate an increasing role of stationary sources in coming years. Mobile sources use light liquid fossil fuels with low levels of chemically bound nitrogen (i.e. <0.05 wt %) and produce predominantly thermal NO_x by high-temperature fixation of atmospheric nitrogen. By contrast, stationary sources also burn large amounts of heavy fuels (coal and residual oil) that contain significant amounts (0.2–1.8 wt %) of chemically bound nitrogen and produce fuel NO_x as well as thermal NO_x. Small-scale experimental studies have indicated that fuel NO_x may account for as much as 90% of the total NO_x from pulverized-coal combustion[1] and 75% of that from heavy-oil combustion[1–3]. It has been estimated that, in the United States, 25% of the combustion-generated NO_x may be attributable to fuel-nitrogen conversion[4].

With experimental combustion systems it has been shown that the fraction of fuel nitrogen converted to NO_x under fuel-lean conditions decreases as the nitrogen content increases, but that the absolute amount of NO_x formed increases[2,5]. This has recently been verified by correlation of some available coal and oil fired combustion data[6]. It has been found that up to 90% reduction of NO_x can be achieved for residual oil and doped distillate oil with staged combustion[2,7]. It was also shown that up to 80% control of total NO_x from coal can be achieved by proper burner design[8]. The results of these small-scale experiments have guided the EPA Industrial Environmental Research Laboratory (IERL-RTP) program in two directions: (1) development and application of NO_x control technology for stationary sources burning coal and heavy oil; and (2) fundamental studies of the chemistry and mechanisms of evolution of nitrogen compounds from real fuels and of subsequent reaction of the nitrogen-containing intermediates. This second type of study should provide valuable guidance for optimization of practical control technology by pointing to methods of enhancing the conversion of the fuel nitrogen to molecular nitrogen.

As a part of the EPA program, a study of the chemical reactions involved in the formation of fuel NO_x is being conducted at Rocketdyne[9]. A portion of this study, reported here, involved the determination of the fate under conditions of inert pyrolysis of synthetic (model) fuel-nitrogen compounds and natural fuel nitrogen contained in fuel oils and coals. The rates of pyrolysis of the model nitrogen compounds were also investigated. Once the fuel is introduced into the combustion zone of a combustor it may experience a wide range of reaction histories including: (1) mixing with air and subsequent reaction at equivalence ratios ranging from rich to lean; (2) devolatilization and pyrolysis under inert, fuel-rich conditions either in a fuel cloud or in the mantle around individual droplets or particles; (3) devolatilization and/or pyrolysis under slightly oxidative conditions as above; and (4) mixing of the devolatilization and pyrolysis products with air and subsequent reaction over a range of stoichiometries. While all of these processes have some elements in common, the actual reaction path of the nitrogen intermediates and the ratio of nitric oxide to molecular nitrogen in the product may be substantially different.

The inert pyrolysis experiments were carried out to investigate the types of reactions that may occur in the fuel-rich preflame zone and to determine if the pyrolysis rates are such that reaction is likely to occur in this zone. The combustion kinetics of the nitrogen species that were found to form under these preflame conditions were then investi-

gated in a premixed CH_4–O_2–Ar flame in another phase of this study[9]. In addition, oxidative pyrolysis studies are currently being carried out by Rocketdyne under EPA Contract 68-02-1886.

An apparent correlation has been demonstrated between the nitrogen contents of petroleum crudes, the carbon residues of the crudes, and the geological period in which the petroleum was formed[10]. Although the total amount of chemically bound nitrogen in fossil fuels is well established, the identities of the specific chemical types are not – particularly for coal nitrogen. It has been determined, however, that much of the nitrogen in heavy oils is in the form of heterocyclic organic compounds[11–15] and the indications are that the same is true for coal nitrogen. About one-third of the nitrogen in petroleum is in the form of basic compounds which are mainly pyridines, pyridans, quinolines, isoquinolines, acridines, phenanthridines, phenazines, pyrazines, and highly substituted pyrroles[16,17]. The remainder is composed of nonbasic compounds which include[18] pyrroles, indoles, carbazoles, benzcarbazoles, amides such as quinolones, and benzonitriles.

The model fuel-nitrogen compounds selected for this study were pyridine, quinoline, pyrrole and benzonitrile. The rationale for using experimentally tractable low-molecular-weight model compounds to represent the highly substituted fuel-nitrogen compounds was that the heterocyclic ring is more thermally stable than the substituted organic groups and, therefore, its rate and mode of reaction may be little affected by the presence of high-molecular-weight substituents[9]. Hurd and coworkers claim to have shown that the methyl pyridines are much less thermally stable than pyridine[19,20]. However, an analysis[9] of their rather crude rate data indicates that the pyrolysis rates of pyridine and the picolines approach each other at the highest temperature of their investigation (850°C). This suggests that the initiation process for the substituted pyridine ring may be the same as for pyridine at the higher heating rates and temperatures encountered in combustion. This would involve either direct ring rupture or loss of a ring hydrogen followed by scission of the pyridyl ring.

Previous studies of the pyrolysis of organic nitrogen compounds have not emphasized determination of the fate of the nitrogen. Johns *et al.*[21] and Hirsch and Lilyquist[22] compared the thermal stabilities of organic compounds and found that the heterocyclic nitrogen compounds are among the most stable. Hurd and Simon[20] pyrolysed pyridine and the three picolines in a flow reactor at 700–850°C under inert conditions. They reported the following product yields from pyridine at 825°C: benzene, 0.18%; acetonitrile, 0.2%; acrylonitrile, 0.4%; benzonitrile, 1.1%; and quinoline, 1.3%. In addition, they observed a large but unmeasured amount of carbonaceous residue. Most of the pyridine-N was not recovered in their measured products. Hurd and Simon reviewed the previous literature on pyridine pyrolysis and noted that hydrogen cyanide had been reported as a product, but no estimate of the amount was given. Ruhemann[23], for example, reported in 1929 that, on increasing the temperature of pyridine decomposition from 600 to 900°C, nuclear scission into hydrogen cyanide becomes important. Hurd and Simon do not mention if they observed hydrogen cyanide from pyridine but state that with the picolines 'hydrogen cyanide was formed in every run above 775°C, but no attempt was made to estimate it quantitatively'.

Pohl and Sarofim[24] have measured the evolution of fuel nitrogen from coals as a function of temperature and heating time. In long-heating-time crucible experiments of the type we have carried out, they observe that the fraction of the fuel nitrogen that is volatilized increases from about 40% at 950°C to about 60% at 1100°C. More than 90% of the nitrogen is driven out of the char at temperatures above 1500°C.

EXPERIMENTAL

These inert pyrolysis experiments were conducted in quartz capillary flow reactors with helium as the carrier gas.

Model-compound apparatus

The model compound reactor consisted of 50 cm of capillary tubing (2.2 mm i.d. x 10 mm o.d.) heated over a 30-cm length. The quartz capillary was attached by graded seals to 1.59-mm (1/16-in) o.d. stainless-steel tubing. Samples of the liquid model compounds, 0.2 μl in size, were injected into a heated port (160°C) where the sample was quickly vapourized and mixed with the flowing helium before entering the reactor. The average concentration of model-compound vapour entering the reactor was about 3 mole %. The reactor pressure, 2.1×10^5 Pa gauge, and the carrier gas mass flowrate, 43 cm^3 (STP)/min, were the same in all model-compound experiments giving a residence time in the heated zone of 0.8 s at 1000°C. The carrier gas leaving the reactor flowed through a minimum-volume line, heated to 160°C, directly to the column of a temperature-programmed gas chromatograph to measure organic products and unreacted model compound. Additional helium was introduced at the head of the column to increase the flowrate to give optimum separation. The conditions in this gas chromatograph were: 60-cm x 3.2-mm Chromasorb 103 column, 83 cm^3 (STP)/min carrier gas flow, 60–250°C at 7.5°C/min, and hydrogen–oxygen flame-ionization detector. Typical retention times were: benzene, 10.8 min; pyridine, 12.8; benzonitrile, 19.2; and quinoline, 24.5. The column was back-flushed after each run to prevent heavier products from eluting later.

The model compound product stream could also be diverted to an ambient temperature line for the measurement of inorganic products. Molecular nitrogen was determined by gas chromatography with a molecular-sieve 5A column (2.75 m x 4.2 mm, 25°C) and thermoconductivity detection. Hydrogen cyanide and ammonia were collected in separate experiments by bubbling the gas stream through 25 ml of rapidly stirred aqueous solution containing either 125 mg of sodium carbonate or 0.01 N hydrochloric acid. The hydrogen cyanide was measured[9] by the ASTM Spectroscopic Cyanide Method D2036-72 in which barbituric acid is used to develop the colour after neutralizing and oxidizing the cyanide to cyanogen chloride with Chloramine-T. Ammonia was determined colorimetrically by the phenate method[25]. Calibration experiments demonstrated that up to 50% of the ammonia was 'absorbed' by the analysis system at the microgram level. Therefore, ammonia yields measured from the model compounds were multiplied by 2 and reported as upper limits. Calibration experiments[9] demonstrated that neither hydrogen cyanide nor ammonia decomposes in a new quartz reactor even at 1100°C (1 s nominal residence time). The interior wall of the model-compound reactor became frosted and began to promote hydrogen cyanide decomposition after several hundred hours of use and had to be replaced.

The carbonaceous residue that formed on the reactor

wall was burned out after each experiment because preliminary results indicated that the residue catalysed the rate of pyrolysis of pyridine (this effect was not studied in detail). The amount of nitrogen contained in the residue was determined in one experiment with pyridine at 960°C. The reactor was removed from the apparatus without burnout and cut to a length that permitted it to be used as the combustion tube in an automatic Dumas nitrogen analyser.

Fuel apparatus

The fuel reactor consisted of a similar quartz capillary (60 cm in length) but had a 2-cm^3 bulb at a point about 10 cm into the 30-cm heated zone. This bulb accommodated the larger volumes of gas generated in the fuel experiments. The quartz reactor was attached to metal Swagelok fittings with Teflon ferrules. Samples of 1.5–2.0 mg of fuel oil or powdered coal were weighed into a miniature quartz boat on the end of a quartz rod which was fitted with a metal extension rod. The thin-walled quartz boat had a semicylindrical opening 8 mm in length x 1.1 mm i.d. The metal rod extended through a rubber septum in the upstream fitting (which had a metal tube soldered to it for introduction of carrier gas) giving a leak-tight seal while allowing the boat to be moved into and out of the preheated reactor.

After first placing the quartz boat containing the fuel sample in a cooled portion of the upstream end of the reactor (external to the furnace), the system was purged for 10 min with flowing helium. The quartz boat was then moved very quickly into the hot reactor to the stop position. The fuel pyrolysed in the boat at the point in the reactor where the capillary began to enlarge to form the bulb, and the volatile products were swept through and out of the reactor by the carrier gas. A removable section of room-temperature stainless-steel tubing attached to the end of the reactor condensed any tar formed during pyrolysis of the fuel samples (both reactors had quartz-wool plugs at the end to trap any carbon particles).

When connected to the molecular sieve gas chromatograph to measure molecular nitrogen, the reactor pressure was 181 kPa gauge and the flowrate 40 cm^3 (STP)/min. Analysis of the volatile decomposition products for hydrogen cyanide involved collection in the aqueous bubbler (over a period of 3 min) using a flowrate of 20 cm^3/min with the reactor at atmospheric pressure. Thus, the residence times in the fuel reactor were similar under these two conditions (about 1.2 s).

The sulphur present in fuels can interfere with the hydrogen cyanide determination. Therefore, it was necessary to suspend cadmium carbonate (40 mg) in the rapidly stirred sodium carbonate collecting solution to prevent reaction of sulphide ions with the cyanide[26]. The insoluble material (cadmium sulphide and cadmium carbonate) was immediately centrifuged out of the solution and the analysis then completed as quickly as possible[9].

The outer surface of the boat and the interior of the reactor bulb became lightly coated with carbon after each fuel experiment, indicating pyrolysis of volatile species. The reactor and quartz boat were burned out at reaction temperature with oxygen after each experiment to remove the carbonaceous residue. In the coal experiments, the reactor and boat had to be lightly etched with 30% hydrofluoric acid solution after every few experiments to remove the residue and ash. The fuel reactor was still passive toward hydrogen cyanide at 1100°C after a long series of fuel-oil experiments, but became catalytic toward hydrogen cyanide after every few coal experiments. Fortunately, etching with hydrofluoric acid did passivate the fuel reactor again toward hydrogen cyanide.

Nearly complete decomposition of ammonia occurred in the fuel reactor at 1100°C after a short period of use in the initial fuel-oil experiments, and lightly etching the reactor with hydrofluoric acid did not eliminate its activity toward ammonia. Therefore, only the sum of the ammonia and molecular nitrogen formed could be measured in the fuel experiments. The sum of ammonia and molecular nitrogen was obtained by passing the product gas stream first through a nickel tube converter heated to 1050°C to decompose to nitrogen any ammonia that survived the reactor. The total molecular nitrogen was then measured with the molecular sieve gas chromatograph. It was necessary to place an Ascarite trap (sodium hydroxide) heated to 140°C after the reactor to remove hydrogen cyanide from the product stream because it also decomposed to molecular nitrogen in the converter. This procedure permitted an upper limit to be placed on the amount of ammonia formed in fuel pyrolysis.

RESULTS AND DISCUSSION

The model fuel-nitrogen compounds were pyrolysed in helium over the temperature range of 850–1100°C at a fixed mass flowrate of carrier gas. The decomposition rates, the major organic products, and the nitrogen-containing inorganic products were measured. Samples of fuel oils and coals were pyrolysed in helium at 950 and 1100°C and the volatile nitrogen-containing inorganic products measured.

Model-compound pyrolysis rates

Compared in *Figure 1* are the extents of reaction of the model compounds as a function of temperature. Pyridine and pyrrole give similarly shaped inert decomposition curves with steep slopes until beyond 95% decomposition. Pyrrole is less stable than pyridine, the 50% decomposition temperature being lower by about 60°C. The quinoline curve is nearly rectilinear with temperature. Benzonitrile is unusual in that its decomposition curve remains steep up to about 960°C and then tails out at high temperatures. 3% of the benzonitrile remains undecomposed even at a temperature of 1100°C. (Since the organic products were identified mainly by their retention times on a gas chromatographic column, the possibility that a very stable product forms that

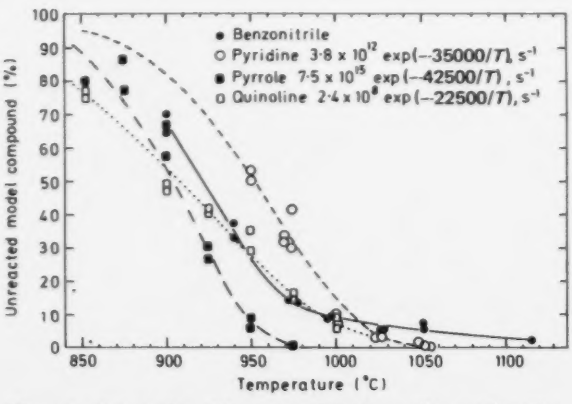

Figure 1 Extent of model-compound decomposition as a function of reactor temperature at constant mass flowrate

Table 1 Kinetic parameters for pyrolysis of model compounds in helium

$-dc/dt = kc^n = Ac^n \exp(-E/RT)$			
Compound	n	$A(s^{-1})$	E(kJ/mol)
Pyridine	1	3.8×10^{12}	293
Pyrrole	1	7.5×10^{15}	356
Quinoline	1	2.4×10^{8}	188

has the same retention time as benzonitrile cannot be ruled out, but no candidate species is apparent. Also, a fast scanning monopole mass spectrometer was used to analyse the GC peak from benzonitrile and only benzonitrile was identified in the spectra.) It can be seen that since the curves cross, the relative thermal stabilities of some of the compounds are a function of temperature.

The experimental decomposition curves in *Figure 1* for pyridine, pyrrole and quinoline were found to fit simple first-order rate expressions with the kinetic parameters listed in *Table 1*. However, the overall rate expression for pyridine was found later to be more complex than this, and the benzonitrile data did not fit any single-order rate expression. The trial rate expressions for each species were integrated[9] through the reactor (taking into account the effects of temperature profile and mole change on gas velocity) until a fit was obtained with the experimental curve. The curves giving the best fits are plotted in *Figure 1*. The rate parameters in *Table 1* obtained for pyridine and pyrrole suggest that the rate-determining step is a unimolecular reaction. Such reactions typically[27] have pre-exponential factors in the range of 10^{13}–10^{16} s^{-1}. The surprising feature is that pyrrole, which is less stable and less aromatic than pyridine, has a higher apparent activation energy for decomposition. The quinoline kinetic parameters suggest a heterogeneous reaction.

One experimental series was conducted with pyridine in which the initial concentration was reduced by about an order of magnitude (by prevapourizing pyridine in a separate helium stream and using a gas sampling valve). Under these conditions, the 50% decomposition temperature for pyridine is about 40°C higher than in *Figure 1*, indicating that the pyridine kinetics are more complex than the initial results suggested and the rate-determining step is not a simple unimolecular reaction. The measured extents of reaction of pyridine under these lower concentration conditions also fit a first-order rate expression with an activation energy of 293 kJ/mol, but the pre-exponential factor is smaller by a factor of three (1.25×10^{12} s^{-1}).

Although the pyridine rate expression in *Table 1* does not hold under all conditions, it has been reported[28] to predict the rate of reaction of added pyridine in the early stages of a premixed flat hydrocarbon–air flame. The extrapolated pyridine half-lives predicted by this expression (in the absence of oxygen) are 4.4 ms at 1200°C, 0.97 ms at 1300°C, 0.25 ms at 1400°C and 0.08 ms at 1500°C, indicating that heterocyclic nitrogen compounds should begin to react rapidly in a diffusion flame at about 1300°C even if the amount of oxygen that has diffused through the flamefront is small.

Model-compound products

The organic products formed from pyridine are plotted in *Figure 2* as a function of the temperature. The nitrogen-containing species are denoted by solid curves. The organic products, excluding methane, account for about 14 wt % of the pyridine reacted at 950°C. This is about 3 times the total organic product yield reported by Hurd and Simon[20] at 825°C. This difference could result from the different temperature range or from the experimental procedures employed. If the residue that accumulated in Hurd and Simon's reactor did catalyse its own formation, the organic yields would be smaller under their conditions. The organic products from pyridine in *Figure 2* are the same as were reported by Hurd and Simon (i.e. benzene, acetonitrile, acrylonitrile, benzonitrile and quinoline) and the yield curves are such that they could well extrapolate to the relative yields obtained by Hurd and Simon at the lower temperature (e.g. quinoline yield slightly greater than benzonitrile). Methane was formed from pyridine in a yield greater than 10 wt % over the entire temperature range.

It cannot be established from the available data if the changes in the pyridine product yield distribution with temperature result mainly from changes in the initial distribution of primary pyrolysis products or from the secondary pyrolysis of the less stable products. However, secondary reactions probably have an appreciable effect. For example, the shape of the benzonitrile curve in *Figure 2* is similar to its high-temperature 'tail' in *Figure 1*. This indicates that, at the higher temperatures, more of the less thermally stable products could have formed in the primary pyrolysis process and then decomposed before leaving the reactor.

Only two major aromatic products form from benzonitrile over the temperature range 975–1120°C. Benzene forms in a 15% yield, dropping off to about 10% at the higher temperatures. A 3% yield of biphenyl forms at 975°C which decreases gradually to 0.5% at 1110°C (a few tenths of a percent of naphthalene also forms at about 1050°C). The formation of benzene and biphenyl as the major organic products is in agreement with the expectation that an initial C–CN bond rupture occurs in benzonitrile. The maximum amount of methane that forms from benzonitrile is 1.5%.

Quinoline appears to form mainly carbonaceous residue over the temperature range of 850–1000°C (based on a carbon mass balance). The three measurable organic products are benzonitrile, increasing from a 1% yield at 850°C to 4% at 980°C; benzene, increasing from 0.7% at 850°C to

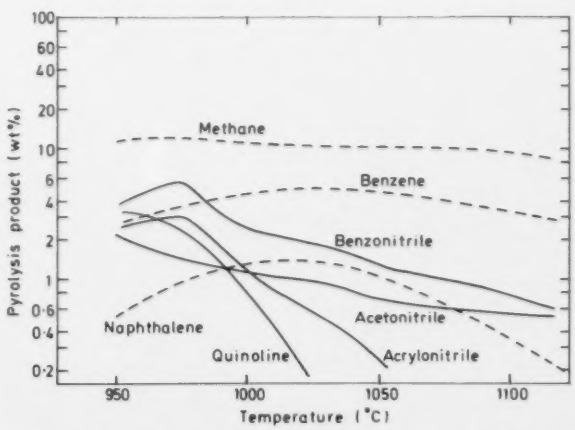

Figure 2 Organic products from inert pyrolysis of pyridine (solid lines denote nitrogen-containing products)

Table 2 Nitrogen balance in inert pyrolysis of pyridine

Product	Nitrogen in product[a] (%)	
	960°C	1100°C
Residue	49	NM[b]
HCN	40	102
Benzonitrile	5	0.5
Quinoline	3	<0.1
Acrylonitrile	3	<0.1
NH_3	<5	NM
N_2	<0.1	NM
	≈100	102

[a] Based on nitrogen in decomposed portion of sample (65% at 960°C and 99.9% at 1100°C)
[b] NM: not measured

about 10% at 1000°C; and methane, increasing from 1% at 850°C to 4% at 1000°C.

The organic products from pyrrole were not studied in as much detail but at 900°C all of the carbon in the reacted pyrrole is recovered in the volatile products. The measured organic yields at 900°C are: 23% methane, 18% acrylonitrile, 15% acetonitrile, 4.5% benzene and 3.5% benzonitrile. In addition, two unknown organic products form in high yield: 11% of a C_2 compound and 28% of a C_5 or C_6 compound (it was assumed that these compounds had the same detector sensitivity as did acetonitrile and pyridine, respectively). The latter has the same retention time in the gas chromatograph as does pyridine. It would be quite unexpected if the major product that forms from the 5-membered heterocyclic ring in pyrrole is the 6-membered ring of pyridine.

The volatile inorganic products were measured from the inert pyrolysis of pyridine and benzonitrile only. The yield of hydrogen cyanide from pyridine (moles formed per mole of pyridine reacted) increases from 40 ± 4% at 960°C to 102 ± 4% at 1106°C. This increase in hydrogen cyanide yield with temperature is in agreement with previous observations[23] but the complete conversion of pyridine to hydrogen cyanide at 1106°C was unexpected. The hydrogen cyanide yield from benzonitrile is 49 ± 4% at 956°C and 82 ± 1% at 1106°C.

Ammonia is formed only in minor amounts under these conditions. An upper limit of 5% ammonia forms from pyridine at 960°C and 8% from benzonitrile. Added ammonia passing over a carbonaceous residue formed in a previous pyridine pyrolysis experiment does not react with the residue at 1050°C to form hydrogen cyanide.

When pyridine or benzonitrile is pyrolysed in this quartz reactor between 950 and 1100°C, no detectable molecular nitrogen is formed (i.e. yield < 1%). In nickel or stainless-steel reactors, however, molecular nitrogen forms from pyridine (the only compound tested) in yields up to 90%.

The nitrogen content of the carbonaceous residue was measured in only one experiment (pyridine at 960°C). This residue contained 49% of the nitrogen from the fraction of the pyridine sample that reacted (two-thirds) and was estimated to contain about half of the carbon (based on unrecovered carbon). This indicates that the residue has about the same nitrogen-to-carbon ratio as in pyridine.

A good nitrogen balance was obtained from pyridine as shown in *Table 2*. At 960°C, half of the pyridine nitrogen is retained in the residue and most of the rest forms hydrogen cyanide; while at about 1100°C, essentially all of the pyridine is converted to hydrogen cyanide (although not necessarily in a single step).

Products from fuel pyrolysis

The volatile inorganic products were measured from the inert pyrolysis of fuel oils and coals. As is the case with the model compounds, the most abundant volatile nitrogen product from the fossil fuels is hydrogen cyanide. Six No. 6 fuel oils and one crude oil were studied. The yields of hydrogen cyanide at 1100°C range from 23 to 50%, *Table 3*, the amount forming from a given oil at 950°C being between half and two-thirds of that forming at the higher temperature. The hydrogen cyanide results reported here correct those reported previously[29]. A cyanide-sensitive electrode method was used in the earlier experimental series and it was found later that there is a sulphur (hydrogen sulphide) interference problem.

The amounts of ammonia and molecular nitrogen (measured together) formed from four of these oils are listed in *Table 4*. The percentage of the fuel nitrogen that is apparently converted to these products is an inverse function of the fuel-nitrogen content. In fact, when the yields of ammonia + nitrogen are reported in micrograms per milligram of fuel (*Table 4*), they are only weakly dependent on fuel-nitrogen content and temperature for oils containing from 0.22 to 1.41% nitrogen. These absolute yields of ammonia + nitrogen are 0.65 ± 0.1 microgram per milligram oil at 950°C and 0.73 ± 0.1 at 1100°C. It is possible that most of this is molecular nitrogen dissolved in the oil samples. The solubility of nitrogen at atmospheric pressure in turbine oil, for example, is 0.3 microgram per milligram. If this is the case, a very low upper limit can be placed on the amount of ammonia formed as a pyrolysis product of oils.

Table 3 Hydrogen cyanide yields from oils under inert pyrolysis conditions

Oil sample	Nitrogen to hydrogen cyanide[f] (%)		
	1100°C	950°C	Ratio
A. No.6 Fuel Oil[a] (Venezuelan Crude) 0.43% N, 2.3% S	32.9 ± 0.6	19.4 ± 0.3	0.59
B. No.6 Fuel Oil[a] (Various Crudes) 0.44% N, 0.73% S	38.8 ± 0.8	23.2 ± 0.1	0.60
C. No.6 Fuel Oil[a] (Mainly California Crudes) 1.41% N, 1.6% S	23.2 ± 0.1	14.5 ± 0.3	0.63
D. No.6 Fuel Oil[b] 0.3% N, 0.7% S	42.0 ± 1.1	20.4 ± 0.6	0.49
E. No.6 Fuel Oil[c] 0.22% N, 0.9% S	37.0 ± 0.3	24.6 ± 0.3	0.67
F. No.6 Fuel Oil[d] 0.38% N, 0.3% S	35.2 ± 0.2	17.8 ± 0.6	0.51
G. Wilmington Crude Oil[e] 0.63% N, 1.6% S	49.8 ± 1.6	30.3 ± 1.0	0.61

[a] Supplied by Gulf Research and Development Co.
[b] Supplied by Conoco
[c] Supplied by Environmental Protection Agency (IERL-RTP)
[d] Supplied by Ultrasystems Corp.
[e] Supplied by U.S. Bureau of Mines, Laramie, Wyo.
[f] Average of duplicate experiments

Table 4 Yields of ammonia + nitrogen (measured together as N_2) from oils under inert pyrolysis conditions

Oil sample	N (wt %)	Fuel nitrogen converted to ammonia + nitrogen (%)		Ammonia + nitrogen formed (microgram per milligram oil)	
		950°C	1100°C	950°C	1100°C
No.6 Fuel Oil (E)[a]	0.22	23.8 ± 0.5	28.2 ± 1.0	0.52 ± 0.01	0.62 ± 0.02
Crude Oil (G)	0.63	10.5 ± 0.8	10.9 ± 0.2	0.66 ± 0.05	0.75 ± 0.01
No.6 Fuel Oil (C)	1.41	5.2 ± 0.8	5.9 ± 0.4	0.73 ± 0.10	0.83 ± 0.05
No.6 Fuel Oil (F)	0.38	–	16.1	–	0.61

[a] Sample No. in *Table 3*

Table 5 Inorganic products from coal pyrolysis

Coal sample	N (wt %)	Fuel-N converted to hydrogen cyanide (%)		Fuel-N converted ammonia + nitrogen at 954°C (%)
		957°C	1106°C	
I[a]	1.17	20.3, 18.0	29.8, 30.2	8.3, 10.5
II[b]	1.8	–	26.2, 22.7	–

[a] A bituminous coal, containing 3% sulphur, supplied by the Environmental Protection Agency (IERL-RTP)
[b] A British bituminous coal supplied by the International Flame Research Foundation

The inert pyrolysis of two coal samples gave the products shown in *Table 5*. The yields of hydrogen cyanide (24 and 30% at 1106°C and 19% at 957°C) are similar to those obtained from the oils. An ammonia + nitrogen yield of about 9% was obtained under the one condition studied. This represents an absolute yield of 1.1 microgram per milligram of coal which is somewhat higher than the absolute yields from the oils.

In addition to the char and residue that remained in the sample boat after the fuel experiments, a thin carbonaceous residue similar to that obtained in the model-compound experiments coated the wall of the enlarged portion of the reactor just downstream from the boat. This residue forms from both coals and oils. It is possible, therefore, that much of the hydrogen cyanide forms from the fuels via the pyrolysis of volatile nitrogen species as was the case with the model compounds. This is being investigated further by Rocketdyne under EPA contract 68-02-1886 using a two-temperature-zone reactor.

The hydrogen cyanide yields from the fuels cannot be compared directly with those from the model compounds because the amount of non-volatile nitrogen remaining in the fuel residues was not measured. An attempt was made to measure this with the two coals, but definitive results were not obtained. It is likely that much of the fuel nitrogen is non-volatile at these temperatures; the results of Pohl and Sarofim[24] have shown this to be the case with coal. Therefore, the volatile fuel-nitrogen compounds form hydrogen cyanide in high yields approaching those of the model compounds. The increase in hydrogen cyanide yield with temperature probably results partly from the increase in volatile nitrogen[24] and partly from the increase in hydrogen cyanide yield from the volatile species as was observed in the model-compound experiments.

CONCLUSIONS

These results indicate that fuel-nitrogen compounds form high yields of hydrogen cyanide when pyrolysed in the absence of oxygen. Since these yields increase with temperature, relatively large amounts of hydrogen cyanide may form in the early stages of a diffusion flame (surrounding a fuel particle or droplet) where the heating rates are quite high. In fact, these results suggest that hydrogen cyanide may be the principal intermediate in the formation of fuel NO_x. These pyrolysis results may provide insight into reaction conditions necessary to evolve fuel-nitrogen intermediates in a controlled manner as a function of reaction-zone conditions and, thereby, optimize fuel NO_x control techniques.

Modelling of the diffusion flame, using the rate constants obtained in this study, will be required to determine at what point the fuel-nitrogen compounds will decompose thermally. They may be so thermally stable that they can survive far enough into the flamefront to react with oxygen species diffusing through the flame before undergoing thermal decomposition. Data on oxidative pyrolysis are required before the competition between these two processes can be modelled.

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REFERENCES

1 Pershing, D. W., Martin, G. B. and Berkau, E. E. (Presented at 66th Annual AIChE Meeting, 1973) *AIChE Symposium Series No. 148*, 1975, **71**, 19
2 Turner, D. W., Andrews, R. L. and Siegmund, C. W. (Presented at 64th Annual AIChE Meeting, 1971) *AIChE Symposium Series No. 126*, 1972, **68**, 55
3 Muzio, L. J., Wilson, R. P. Jr and McComis, C., 'Package Boiler Flame Modifications for Reducing Nitric Oxide Emissions – Phase II of III', *EPA-R2-73-292b (NTIS No. PB 236752/AS)*, June 1974
4 Flagan, R. C. *PhD Thesis*, Massachusetts Institute of Technology, 1973
5 Martin, G. B. and Berkau, E. E. (Presented at 64th Annual AIChE Meeting, 1971) *AIChE Symposium Series No. 126*, 1972, **68**, 45
6 Dykema, O. W. and Hall, R. E., 'Analysis of Gas-, Oil-, and Coal-Fired Utility Boiler Test Data', pp IV-115 to -162, *Proc. Stationary Source Combustion Symposium, Vol. III. Field Testing and Surveys, EPA-600/2-76-152c (NTIS No. PB 257146/AS)*, June 1976
7 Martin, G. B. and Berkau, E. E., presented at *14th Symposium (Int.) on Combustion*, 1972

8 Heap, M. P., Lowes, T. M., Walmsley, R. and Bartelds, H. 'Burner Design Principles for Minimum NO_X Emissions', pp 141–171, *Proc. Coal Combustion Seminar,* June 19–20, 1973, *EPA-650/2-73-021 (NTIS No. PB 224210/AS),* Sept. 1973

9 Axworthy, A. E., Schneider, G. R., Schuman, M. D. and Dayan, V. H. 'Chemistry of Fuel Nitrogen Conversion to Nitrogen Oxides in Combustion', *EPA-600/2-76-039 (NTIS No. PB 250373/AS),* Feb. 1976

10 Ball, J. S., Whisman, M. L. and Wenger, W. J. *Ind. Engng Chem.* 1951, **43**, 2577

11 Albert, D. K. *Anal. Chem.* 1967, **39**, 1113

12 Brandenburg, C. F. and Latham, D. R. *J. Chem. Engng Data* 1968, **13**, 391

13 Drushel, H. V. and Sommers, A. L. *Anal. Chem.* 1966, **38**, 19

14 Snyder, L. R., Buell, B. E. and Howard, H. E. *Anal. Chem.* 1968, **40**, 1303

15 Snyder, L. R. *Anal. Chem.* 1969, **41**, 314

16 Haines, W. E., Cook, G. L. and Dinneen, G. U., Paper presented at 7th World Petroleum Congress, Prague, 1967

17 Richter, F. P., Caesser, P. D., Meisel, S. L. and Offenhauer, R. D. *Ind. Engng Chem.* 1952, **44**, 2601

18 Lathan, D. R., Okuno, I. and Haines, W. E. *Hydrocarbon Analysis, ASTM STP 389,* Amer. Soc. Test. Mat. 1965, 385

19 Hurd, C. D., Macon, A. R., Simon, J. I. and Levetan, R. V. *J. Am. Chem. Soc.* 1962, **84**, 4509

20 Hurd, C. D. and Simon, J. I. *J. Am. Chem. Soc.* 1962, **84**, 4519

21 Johns, I. B., McElhill, E. A. and Smith, J. O. *J. Chem. Engng Data* 1962, **7**, 277

22 Hirsch, S. S. and Lilyquist, M. R. *J. Appl. Polymer Sci.* 1967, **11**, 305

23 Ruhemann, S. *Braunkohle,* 1929, **28**, 749

24 Pohl, J. H. and Sarofim, A. F. *16th Symposium (Int.) on Combustion,* 1976, p 491

25 *Standard Methods for the Examination of Water and Wastewater,* 13th edn, Amer, Public Health Assoc., 1971, p 232

26 Hiiro, K. and Yamamoto, Y. *Anal. Letters* 1963, **6**, 761

27 Benson, S. W. *Thermochemical Kinetics,* John Wiley, New York, 1968

28 Levy, A. Battelle Columbus Research Laboratory, private communication, 1974

29 Axworthy, A. E. (Presented at 66th Annual AIChE Meeting, 1973) *AIChE Symposium Series No.148,* 1975, **71**, 43